

FOOD STORAGE STABILITY

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Mathematical modeling of quality loss

Edward W. Ross

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Introduction

The purpose of this chapter is to present and discuss some of the most important examples of mathematical modeling as they relate to changes in quality during food storage. No universal mathematical theory exists that can be used to model all quality changes in foods. The variety of mechanisms and phenomena is too great to be encompassed within any single, usable set of equations. Although we describe a general framework for such a theory in the next section, it is too general and vague to be of much immediate help in practical situations, and we are forced to specify the theory more narrowly in order to make it applicable.

The word "quality," as used in descriptions of food, can be interpreted in many ways. A consumer may perceive the food as of high quality for a number of reasons, and a food scientist may make a similar (or contradictory) judgment for different reasons. In this chapter we do not define quality precisely but leave it as a somewhat intuitive concept. Further discussion of the definition can be found in some of the other sections of this book, especially Chapters 2 and 12.

The quality of foods, however defined, is assumed to be capable of change with the passage of time. The scale of the time change may be short (e.g., minutes, during

processing) or long (e.g., months, during storage). The agents causing the quality change are usually physical, chemical, or biological and may act in extremely complicated combinations. Often, temperature is the single, dominant factor, but the change may also be affected by the presence of moisture, oxygen, and bacteria of many kinds. The main part of the review deals with the situation where there is a single, dominant variable (say, temperature) whose time variation is known. The problem of finding the time variation of the dominant variable is not discussed here.

There is an intimate relationship between the mathematics involved in estimating quality loss and that involved in the study of food-processing methods. The quality loss during storage may be regarded as a form of processing at relatively low temperatures but going on for rather long times. It is natural that many of the concepts developed in connection with food processing will play similar roles in a quality-loss context, and so quantities such as z , Q_{10} and F_0 are important to us.

The literature dealing with this subject is large, and we make no attempt to cite all or even most of it. Some references that the author has found valuable are given in the bibliography at the end of this chapter. Any review of a technical field is bound to reflect the viewpoint of the author, and the present one is no exception. The main intention here is to describe a version of the existing theory which (the author believes) offers the best basis for future work in the field. Undoubtedly this slights many worthwhile contributions of others in this field, a flaw which the author regrets but cannot correct within existing limitations of space.

General theory

The quality is assumed to be defined numerically in some way as the quantity A , a function of time, t , and possibly also of spatial position, x . The latter dependence will not play a major role in what follows, but, if food is stored in a large mass, it may be necessary to consider it. We define also $v_1(t, x), v_2(t, x), \dots, v_m(t, x)$ as the variable agents of change. For example, $v_1(t, x)$ might be the temperature, $v_2(t, x)$ moisture content, etc. Any of these quantities may also involve constants or parameters, which we collectively denote by P . Then it is reasonable to think that the quality change is governed by some mathematical model of the general form

$$\begin{aligned} dv_1/dt &= \Psi_1(A, v_1, v_2, \dots, v_m, P) \\ dv_2/dt &= \Psi_2(A, v_1, v_2, \dots, v_m, P) \\ &\vdots \\ dv_m/dt &= \Psi_m(A, v_1, v_2, \dots, v_m, P). \end{aligned}$$

This system of ordinary differential equations is to be solved with initial conditions at time t_0 :

$$\begin{aligned} A(t_0) &= A_0, \quad v_1(t_0) = v_{10}, \\ v_2(t_0) &= v_{20}, \quad \dots, \quad v_m(t_0) = v_{m0}. \end{aligned}$$

In the differential equation system we usually assume that the quantities on the left and right sides of the equality signs are to be evaluated at the same time, t . However, it may

occasionally be desirable to evaluate some of the quantities on the right side at an earlier time, in which case the model is said to be of differential-delay or differential-difference form. We do not pursue that case in the present chapter.

This system is too general to be useful. It must be specialized by choosing the functions $\Psi_0, \Psi_1, \Psi_2, \dots, \Psi_m$ and the parameters, P . An example of a system which is more specific but still general enough to contain many commonly used models is obtained by assuming that $m = 2$ and making the definitions

$$\Psi_0 = v_1 \alpha(A, P)$$

$$\Psi_1 = \Psi_2 \, d\beta/dv_2$$

and $v_1(t_0) = \beta(t_0)$. Then the model equations become

$$dA/dt = v_1 \alpha(A, P)$$

$$dv_1/dt = \Psi_2(v_2) \, d\beta/dv_2$$

$$dv_2/dt = \Psi_2(v_2).$$

The function α may be any reasonable function of A containing parameters P , and β is any reasonable function of v_2 . If Ψ_2 is eliminated between the last two equations, and the chain-rule used, we obtain in place of the second equation

$$dv_1/dt = d\beta/dt.$$

If this is integrated and the initial condition used, we see that the above differential equation for v_1 can be replaced by

$$v_1 = \beta = \beta[v_2(t)].$$

This system may be regarded as a prototype for the models used in estimating shelf life and quality loss.

To see how this model reduces to a familiar form, define

$$\pm v_1 = \pm \beta = k = \text{the rate constant}$$

$$v_2 = T = \text{absolute temperature, degrees Kelvin}$$

$$\alpha(A, P) = A^n.$$

and the symbol P is taken as the lone parameter n , the order of the process. Then the model becomes

$$dA/dt = \pm k[T(t)] A^n$$

$$dT/dt = \Psi_2(T).$$

The latter of these equations simply determines the function $T(t)$, the temperature history which the food experiences. Henceforth, we assume that the temperature history, $T(t)$, is

known, and so it is unnecessary to consider the last equation further. The form of the function $k[T]$ specifies the kinetics of the process, which will be discussed later.

In the following derivation, the quality A is assumed to obey the above differential equation,

$$dA/dt = \pm k A^n \quad (k \geq 0, n \geq 0),$$

and the initial condition $A(t_0) = A_0$. That is, A obeys an n -th order process. The rate function, k , has dimension (dim) given by

$$\dim k = (\text{time})^{-1} (\dim A^{1-n}).$$

The rate function k may depend on many variables, e.g., temperature, moisture, oxygen level, and any of these may itself depend on time. We assume that one of these variables is dominant, that the dominant one is temperature, $T(t)$, and that $T(t)$ is known. However, the derivation is quite general and applicable if the dominant variable is not temperature but some other variable or combination of variables, as long as the time dependence of that variable is known. It is easily verified that, if $k = k[T(t)]$, the time dependence of the solution to the differential equation can be expressed in terms of

$$\phi(t) = \int_{s=t_0}^{s=t} k[T(s)] ds, \quad (1)$$

and the solution can be written

$$A(t)/A_0 = [1 - c A_0^{-c} \phi(t)]^{1/c} \quad \text{for } c \neq 0 \quad (2)$$

$$= e^{[-\phi(t)]} \quad \text{for } c = 0. \quad (3)$$

Here $c = 1 - n$, and so $c \leq 1$.

The time dependence of A is entirely governed by the behavior of $\phi(t)$, which is a nondecreasing function of t with $\phi(t_0) = 0$.

The above solutions may be expressed in terms of the quantities

$R(t)$ = fraction of quality remaining at time t

$$= A(t)/A_0$$

$D(t)$ = fraction of quality lost by time t

$$= 1 - R(t) = [A_0 - A(t)]/A_0$$

as

$$R(t) = 1 \pm D(t) = G[\phi(t); c, A_0]$$

in which

$$\begin{aligned} G[\phi(t); 0, A_o] &= e^{\pm\phi(t)} & \text{for } c = 0 \\ G[\phi(t); c, A_o] &= [1 \pm c A_o^{\pm c} \phi(t)]^{1/c} & \text{for } c \neq 0. \end{aligned}$$

The simplest situation is that of constant temperature, say $T = T_o$, and $k = k_o = k(T_o)$, for which case

$$\phi(t) = k_o(t \pm t_o)$$

is to be substituted in the preceding equations. We may then write the solutions in several important circumstances as follows: For $n = 0$, $c = 1$, a zero-order process,

$$\begin{aligned} R(t) &= A(t)/A_o = 1 \pm \phi/A_o = 1 \pm k(t \pm t_o)/A_o \\ A(t) &= A_o \pm \phi = A_o \pm k(t \pm t_o). \end{aligned}$$

For $n = 1$, $c = 0$, a first-order process,

$$\begin{aligned} R(t) &= \exp[\pm\phi] = e^{\pm k(t \pm t_o)} \\ A(t) &= A_o \exp(\pm\phi) = A_o e^{\pm k(t \pm t_o)} \end{aligned}$$

The change in form between the cases $c = 0$ and $c \neq 0$ is sometimes inconvenient, and it is useful to have a formula that displays explicitly the behavior of A in the case where $|c|$ is small. One such formula can be found by expanding ϕ in powers of c , equating coefficients and neglecting all terms after the first correction in the general solutions. The result is

$$\begin{aligned} R(t) &= A(t)/A_o \approx e^{\pm\phi(t)\{1+\tau(t)\}} \\ \tau(t) &= (1/2)\phi(t) \pm \ln A_o. \end{aligned} \tag{4}$$

The formula is accurate only when $|c|$ is small but shows how the transition occurs between the cases $c = 0$ and $c \neq 0$.

The behaviors of these solutions in more-or-less typical situations are displayed in Figures 1 through 3. In these graphs the remaining quality, R , is shown as a function of t (hours) for various values of the parameters. The temperature, T , is assumed constant, and A is taken to have the initial value $A = A_o = 100$ at time $t = t_o = 0$. For this special case the parameters are c (i.e., the order) and k_o . Figure 1 shows the effect on $R(t)$ of varying c for a fixed $k_o = k = 0.1$. The effect of changes in k for fixed c are illustrated in Figure 2, and Figure 3 displays a comparison between exact solutions, Equations (2) and (3), and approximate solutions, Equation (4), for small c .

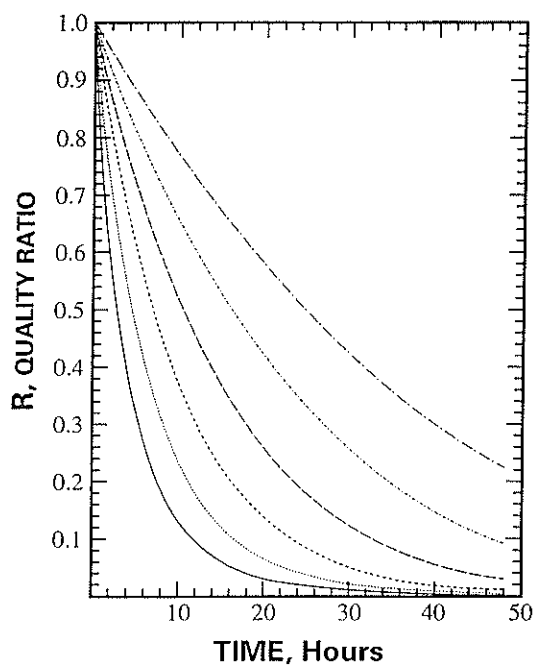


Figure 1 R as a function of time, t , in hours for $k = 0.1$ and various values of c . (---), $c = 0.3$; (-.-.-), $c = 0.2$; (- - - -), $c = 0.1$; (---), $c = 0$; (.....), $c = -0.1$; (- - - - -), $c = -0.2$.

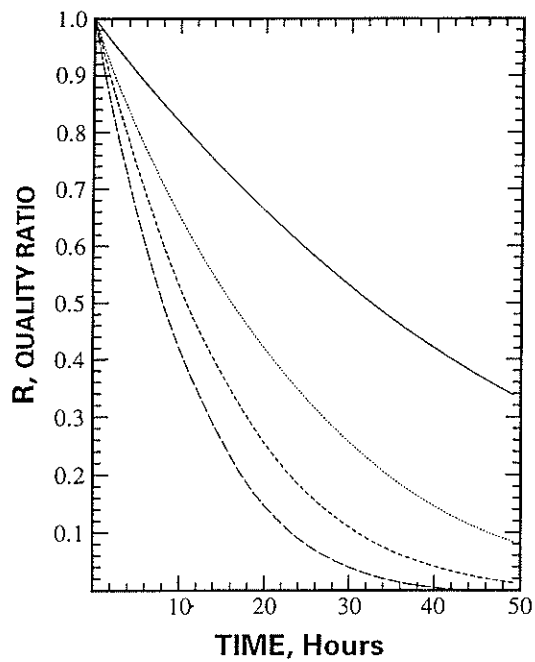


Figure 2 R as a function of time, t , in hours for $c = 0.2$ and various values of k . (---), $k = 0.2$; (-.-.-), $k = 0.15$; (.....), $k = 0.1$; (- - - -), $k = 0.05$.

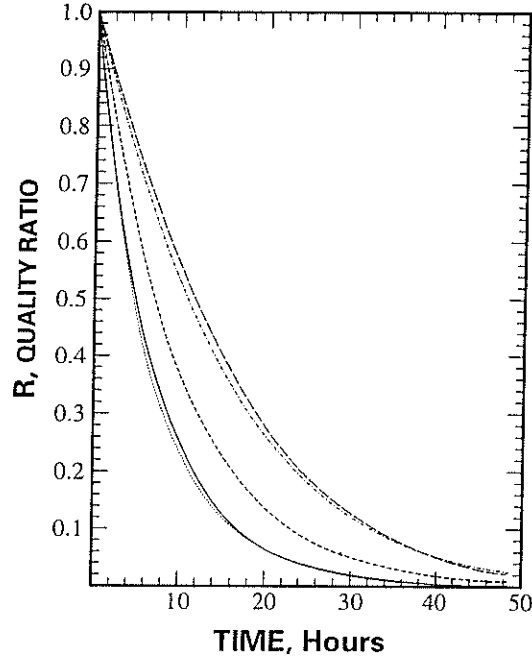


Figure 3 R as a function of time, t , in hours for $k = 0.1$ and small values of c . Comparison of exact solution, Equation (2), with approximate solution, Equation (4). (---), $c = 0.1$, exact; (- - - -), $c = 0.1$, approx.; (- - - -), $c = 0$, exact and approx.; (.....), $c = -0.1$, exact; (-----), $c = -0.1$, approx.

Shelf life

We define the lowest acceptable value of A as A_b . If A declines to or below A_b , the quality is assumed to be unacceptable. The time at which this happens is t_b , and the shelf life is

$$L = t_b \pm t_o.$$

If $\phi(t)$ is a strictly increasing function ($d\phi/dt > 0$), t_b and L are unique. If $R_b \equiv R(t_b)$, the value of t_b is found by solving for t the equation

$$R(t) = R_b.$$

This condition can also be expressed as

$$G[\phi(t_b); c, A_o] = R_b,$$

or, solving for $\phi(t_b)$,

$$\phi_b = \phi(t_b) = W(R_b, c, A_o), \quad (5)$$

provided we define the function W to be

$$\begin{aligned} W &= A_o^c (1 \pm R_b^c) / c && \text{for } c \neq 0 \\ &= \pm \ln R_b && \text{for } c = 0. \end{aligned}$$

The values of t_b and L depend on c , R_b , A_o , (if $c \neq 0$) and very much on the form of $\phi(t)$. In the special but important case where T is constant, and so k is constant, $k = k_o$, and $c \neq 0$ we have to solve

$$k_o(t_b \pm t_o) = W = A_o^c (1 \pm R_b^c) / c, \quad (6)$$

which leads to

$$L = A_o^c (1 \pm R_b^c) / (ck_o). \quad (7)$$

When $c = 0$, we obtain

$$L = \pm (1/k_o) \ln(R_b). \quad (8)$$

Similarly, an approximate formula for the shelf-life when $|c|$ is small and T constant can be found from Equation (4) by solving

$$\pm \ln R_b = \phi_b (1 \pm c \ln A_o) + c \phi_b^2 / 2$$

for $\phi_b = k_o L$. After some simplification the formulas

$$\begin{aligned} L &= \phi_b / k_o \\ \phi_b &\approx \pm (\ln R_b) \left[1 + c \ln(A_o R_b^{1/2}) \right] \end{aligned}$$

are found.

When T is constant, it is clear that the shelf life, L , depends inversely on k_o in all cases considered here. The dependence on c and R_b is illustrated in Figure 4 for the case where $A_o = 100$. In general, L increases as c increases and R_b decreases.

Arrhenius kinetics

In this section we discuss the dependence of k on $T(t)$, i.e., the kinetics, an aspect of the problem that we have largely ignored up till now. It is assumed in what follows that $T(t)$, the absolute temperature history of the food, is known. In practice it is often difficult to find or calculate this function, but for the purposes of the present exposition these obstacles are ignored.

The most common assumption about the behavior of k is embodied in Arrhenius kinetics, i.e., in the assumption that

$$k = k_1 e^{\left[\pm E_a / \{R_g T(t)\} \right]}$$

where k_1 = the pre-exponential constant, E_a = the activation energy, and R_g = the universal gas constant.

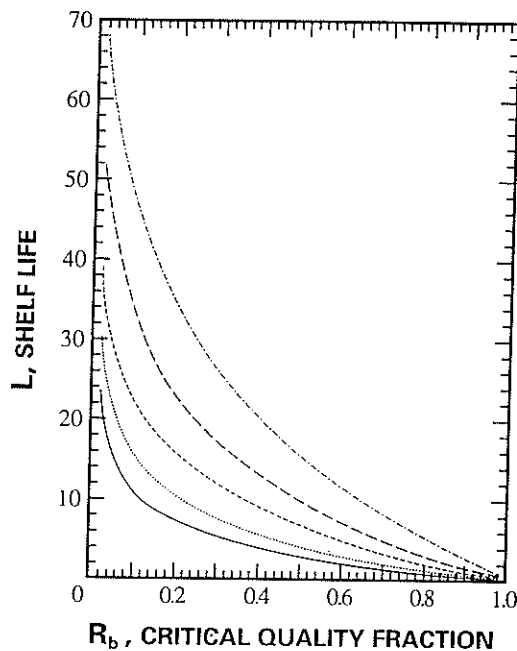


Figure 4 Dependence of shelf life, L , on critical R , R_b , for $k = 0.1$ and various values of c . (---), $c = 0.2$; (-.-.-), $c = 0.1$; (—), $c = 0$; (.....), $c = -0.1$; (-----), $c = -0.2$.

This can be expressed in a slightly different form as follows:

$$k = k_r e^{\left[\frac{\pm E}{R_g T} \pm 1\right]}$$

$$E = E_a / (R_g T_r)$$

$$k_r = k_1 e^{\left[\frac{\pm E_a}{R_g T_r}\right]}$$

T_r is assumed to be a "standard" or "reference" temperature at which the rate is known to be k_r . It is clear that $k = k_r$ when $T = T_r$. In a food-processing context T_r is typically 394.1 K, corresponding to 250°F. In almost all food-storage situations, reasonable values for T_r would lie in the range $250 < T_r < 350$. The parameter E may be regarded as a dimensionless version of the activation energy. Since $R_g \approx 2$, and usually $E_a > 10,000$ cal/mol, the values of E commonly exceed 15 and may reach 100 or more.

For many purposes it is convenient to define

$$x(t) = [T_r/T(t)] \pm 1 \quad \text{or} \quad T(t) = T_r/[1 + x(t)],$$

in which case we can express the Arrhenius Law as

$$k = k_r e^{\pm E x(t)} \quad (9)$$

In this form $x(t)$ is a dimensionless function of temperature. Notice, however, that $x(t)$ is, loosely speaking, "inverse" to temperature: $x(t)$ increases when T decreases and conversely. Figure 5 shows the relation between x and T/T_r , the absolute temperature ratio. As T

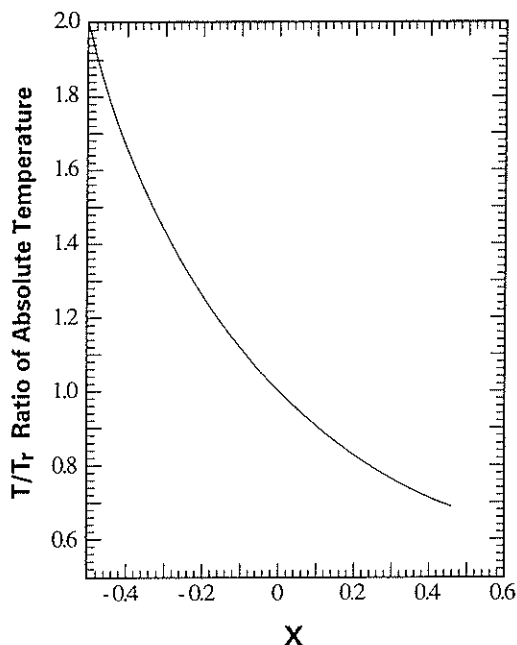


Figure 5 Relation between absolute temperature ratio, T/T_r and x .

decreases, x increases, and $-Ex$ becomes large and negative, implying that k gets smaller, and the process slows down. When $x = 0$, $T = T_r$ and $k = k_r$. If logarithms are taken of both sides in the above equation, we obtain

$$\ln k = \ln k_r \pm Ex$$

Thus, a plot of $\ln k$ versus x will be a straight line with slope $= -E$ and y -intercept $= \ln k_r$.

If T changes over a narrow enough range in the vicinity of T_r then $|x| \ll 1$, and a binomial approximation shows that

$$T \approx T_r(1 \pm x).$$

Therefore, T and x are approximately related in linear fashion as long as the temperature range is not too great, as can be seen in Figure 5. It is also true that, if $|x|$ is sufficiently small, Equation (9) can be approximated by using a Taylor series to obtain

$$k \approx k_r[1 \pm Ex].$$

However, this is inaccurate unless $Ex \ll 1$; since E is usually quite large, this approximation is good only when x is extremely small, i.e., T is very near T_r .

After making the above definitions, the important quantity $\phi(t)$ can be expressed as

$$\phi(t) = k_r F(t)$$

$$F(t) = \int_{s=t_0}^t e^{\pm Ex(s)} ds = \int_{s=t_0}^t 10^{\pm Ex(s)/B} ds$$

$$B = \ln 10 \approx 2.303.$$

The function $F(t)$ always has the dimension of time. If T is constant and equal to T_r between times t_o and t , then $x = 0$ over the entire range of integration, and

$$F(t) = t \pm t_o.$$

$F(t)$ is therefore the elapsed time at temperature T_r . The time dependence of the quality loss is governed only by $\phi(t)$ or $F(t)$. If $T(t)$ and $x(t)$ are variable, $F(t)$ is the time at temperature T_r that produces the quality loss caused by the changing temperature. If the storage or process starts at time t_o and ends at time t_e , then it is usual to call $F(t_e) = F_o$, the equivalent processing time at the reference temperature. Commonly the term F_o is used in a food-processing context only when the reference temperature is 250°F and refers to a complete process. Here, in a food-storage context we shall use $F(t)$ and $F_o(t)$ interchangeably to mean the processing time at the reference temperature (whatever that temperature may be) that is equal to the integral from t_o to t of $e^{[-Ex(s)]}$.

With these definitions the shelf life can be expressed as follows: the time, t_b , at which the quality becomes unacceptable is found by solving Equation (5),

$$\phi(t_b) = k_r F(t_b) = W,$$

which leads to

$$t_b = \phi^{-1}(W) = F^{-1}(W/k_r). \quad (10)$$

Then

$$L = t_b - t_o.$$

Frequently, it is difficult to solve the above equation and find t_b explicitly even if we know the temperature history, $T(t)$. However, it is possible to do this in a few cases, and an example is given later in this chapter.

In dimensionless form the Arrhenius Law can be written

$$k = k_r 10^{\pm Ex/B}$$

A quantity that is often used in defining food processing is the z -value, defined with reference to T_r as follows: $-z$ is the decrease in temperature required to reduce k_r to $k_r/10$. It is easily seen that the x which satisfies that condition is

$$x = B/E$$

corresponding to the temperature

$$T = T_r E / (E + B) = T_z.$$

The definition of z implies

$$T_z = T_r \pm z,$$

which combines with the preceding equation to give

$$z = T_r B / (E + B).$$

If $E \gg B$, as is often the case, this simplifies to the familiar form

$$z \approx T_r B / E = B R_g T_r^2 / E_a.$$

This relationship states that as activation energy increases, smaller reductions in temperature are needed to reduce the rate to (1/10)th of its original value. Notice that z is approximately, but not exactly, proportional to $1/E_a$.

The Q_{10} value

Another quantity that has been defined and studied in connection with food processing is Q_{10} , defined as

$$Q_{10} = \frac{[\text{Rate at Celsius temperature } (h + 10)]}{[\text{Rate at Celsius temperature } h]}$$

where h is the temperature in °Celsius. Q_{10} is usually described as a measure of the sensitivity of the reaction to temperature change. The activation energy, E_a , and its dimensionless counterpart, E , are also measures of the same sensitivity, so it is reasonable that there is a relation between Q_{10} and E_a .

Instead of examining this relationship for Q_{10} , we generalize the definition slightly by defining

$$Q_\delta = \frac{[\text{Rate at Celsius temperature } (h + \delta)]}{[\text{Rate at Celsius temperature } h]} = \frac{k(h + \delta)}{k(h)}$$

δ is the temperature difference in degree Celsius. Since T is the temperature in degrees Kelvin,

$$h = T \pm S, \quad S = 273^\circ.$$

The relation between Q_δ and E_a may be found by using

$$\begin{aligned} Q_\delta &= k(h + \delta) / k(h) = k(T \pm S + \delta) / k(T \pm S) \\ &= \frac{k_1 \exp \left[\pm (E_a / R_g) (T \pm S + \delta)^{-1} \right]}{k_1 \exp \left[\pm (E_a / R_g) (T \pm S)^{-1} \right]}, \\ \ln Q_\delta &= E_a \delta / \left[R_g (T \pm S) (T \pm S + \delta) \right] \\ &= E_a \delta / \left[R_g h (h + \delta) \right], \\ \log_{10} Q_\delta &= E_a \delta / \left[R_g B h (h + \delta) \right]. \end{aligned}$$

If $\delta = 10$, we obtain

$$\begin{aligned}\log_{10} Q_{\delta} &= \left\{10/\left(R_g B\right)\right\} E_a / \{h(h+\delta)\} \\ &\approx 2.19 E_a / \{h(h+\delta)\},\end{aligned}$$

If, instead, it is true that $\delta \ll h$, then

$$\log_{10} Q_{10} \approx E_a \delta / \left[R_g B h^2\right].$$

If the temperature is constant, say h , and the shelf life and rate are $L(h)$ and $k(h)$, respectively, Equation (6) implies

$$k(h) = W/L(h).$$

Similarly, at temperature $h + \delta$,

$$k(h + \delta) = W/L(h + \delta),$$

and so the definition of Q_{δ} implies

$$Q_{\delta} = L(h)/L(h + \delta).$$

Statistical determination of shelf life

Usually, two kinds of information are needed in order to estimate the shelf life of a food, namely, the temperature history and the food parameters. Here we shall focus on the problem of determining the food parameters by experimental and statistical means. We assume throughout this section that the kinetics are of Arrhenius form, as is usually done. Then the parameters that we must determine are c (or n), E (or E_a), k_r and possibly A_0 , the initial quality.

The experiments commonly consist of measurements of quality at various times and constant temperatures. If the times are designated as t_1, t_2, \dots, t_N and the temperatures as T_1, T_2, \dots, T_M , the data can be arranged in an array or spreadsheet as follows:

Time Temp =	T_1	$T_2 \dots T_M$
t_1	A_{11}	A_{12}
t_2	A_{21}	A_{22}
\vdots	\vdots	\vdots
t_N	A_{N1}	A_{N2}

The entry in the i -th row and j -th column is the quality measurement at time t_i and absolute temperature T_j . The entries in the first column, A_{1j} , describe the experimentally obtained

time-variation of quality at the constant temperature T_j , and so on. From these measurements we want to find estimates of c , E , k_r and A_o , based on the formulas described in previous sections.

Since we assume Arrhenius kinetics and constant temperature in each column of the spreadsheet, the function $\phi(t)$ can be expressed for the j -th column (j -th temperature, T_j , or x_j), and i -th time, t_i , as

$$\phi_j(t_i) = k_j(t_i \pm t_o)$$

$$k_j = k_r e^{(\pm E x_j)}$$

If we also assume $t_o = 0$, the entry A_{ij} in the spreadsheet should be of the form

$$\begin{aligned} A_{ij} &= (A_o^c - c k_j t_i)^{1/c} && \text{if } c \neq 0 \\ &= A_o e^{-k_j t_i} && \text{if } c = 0 \end{aligned}$$

Determination of the parameters is usually carried out by doing statistical regression calculations based on these models.

The procedures for estimating the parameters are affected by what is assumed to be known. The simplest situation is that in which the order, i.e., c , is taken as given. In that case only linear regressions have to be done; otherwise, nonlinear regression calculations are usually required, and the computational burden becomes considerable. In the next paragraph we summarize the regression procedures when c is known. In all these cases a two-stage regression procedure is described, in which each temperature is first treated separately to find A_o and k_j , and then the results for k_j at the different temperatures are combined to estimate k_r and E . This appears to be the most commonly used method.

If $c = 0$ (a first-order process), the regression is based on the model found by taking the natural logarithm of the above model for $c = 0$, which gives the model

$$\ln(A_{ij}) = \ln(A_o) - k_j t_i.$$

If a general, linear regression for U as a function of t has model

$$U_i = B_o + B_1 t_i,$$

then the regression for $c = 0$ and $T = T_j$ consists of choosing

$$U_i = \ln(A_{ij})$$

and finding B_o and B_1 by the usual linear-regression procedure. Then

$$\begin{aligned} B_o &= \ln A_o && \text{or } A_o = e^{B_o} \\ B_1 &= -k_j && \text{or } k_j = -B_1 \end{aligned}$$

The usual regression procedure also furnishes estimates of σ , the error standard deviation, and the standard errors in B_0 and B_1 .

If $c \neq 0$, the model can be found by taking the c -th power of each side in Equation (2) to obtain

$$A_{ij}^c = A_0^c \pm ck_j t_i.$$

The usual regression method is performed with

$$U_i = A_{ij}^c$$

and then

$$\begin{aligned} B_0 &= A_0^c & \text{or} & & A_0 &= B_0^{1/c} \\ B_1 &= \pm c k_j & \text{or} & & k_j &= \pm B_1/c. \end{aligned}$$

Again the various standard deviations are also estimated. The simplest such case is $c = 1$ (a process of order zero), for which the regression consists merely of fitting straight lines to the plots of the data, A_{ij} versus t_i , for each j .

Having found estimates of k_j for each j , the quantities k_r and E are found by doing a linear regression based on the model

$$\ln k_j = \ln(k_r) \pm Ex_j$$

which results from taking the natural logarithm of Equation (9). The general linear regression model has

$$U_j = B_0 + B_1 x_j,$$

where

$$U_j = \ln(k_j),$$

After finding B_0 and B_1 by regression, k_r and E are found from

$$\begin{aligned} B_0 &= \ln k_r & \text{or} & & k_r &= e^{B_0} \\ B_1 &= \pm E & \text{or} & & E &= \pm B_1 \end{aligned}$$

The usual regression method once more gives estimates of σ and the standard deviations of B_0 and B_1 . The above descriptions are all based on the assumption that c is known in advance. In practice the data are usually subjected to preliminary visual checks, to see whether the graphs support the claim that c has the hypothesized value. These "eyeball" checks are valuable, but it is questionable whether they can detect modest departures from the assumed value of c . It may be desirable, therefore, to subject the data to a further

analysis by nonlinear regression, in which the four parameters c , A_0 , k_r and E are all sought at the same time. An example of such a calculation has been presented by Haralampu et al.² Also, a recent paper by Rhim et al. takes a step in this direction and is a departure from the usual approach in assuming that tests are conducted with linearly varying temperature.¹²

The conventional two-stage process described above is slightly open to questions of interpretation since the intermediate quantities k_j are treated as data in the second stage but are really quantities derived from the data of the first stage. It is not likely that much error in E or k_r is caused by this, but it appears to miscalculate some of the correlations among the parameters and hence some of the error estimates. Again, more study is needed on the question, and this also suggests that nonlinear regression be undertaken in spite of its computational demands.

Shelf life at variable temperature

An important problem in shelf life estimation is that of finding the effect of temperature variation. In principle, if the temperature history of the food is known, the quantity

$$\phi(t_e) = k_r \int_{t_0}^{t_e} e^{\pm Ex(t)} dt$$

can always be calculated, using numerical integration if necessary. The shelf life, L , is then determinable by solving the equation $\phi(t_e) = k_r F(t_e) = W$ for t_e , provided the parameters of the food are known. If Arrhenius kinetics are assumed, and E is known, $F(t_e)$ becomes

$$F(t_e) = \int_{t_0}^{t_e} e^{\pm Ex(t)} dt$$

The process of determining L is relatively easy when the temperature is constant during storage (i.e., x is constant) but is somewhat more taxing if x varies. While the solution can usually be found by numerical approximations, these are not always helpful in understanding the effects of changes in the parameters or the temperature history. For the latter purpose it would be useful to have exact or accurate approximate solutions, from which the influence of these changes could be seen.

A small number of viable formulas are known, some of which have been obtained by assuming that the temperature range is narrow enough so that T and x are approximately related in linear fashion:

$$x = 1 - (T/T_r).$$

Some results that are accurate over a wider temperature range are given by Rhim et al.¹² Rather than describing these solutions, we shall present a different example of an exact formula that is valid over any physically meaningful temperature range, provided the pulse has the assumed shape. This solution will be used later in the present chapter to illustrate the calculation of shelf life.

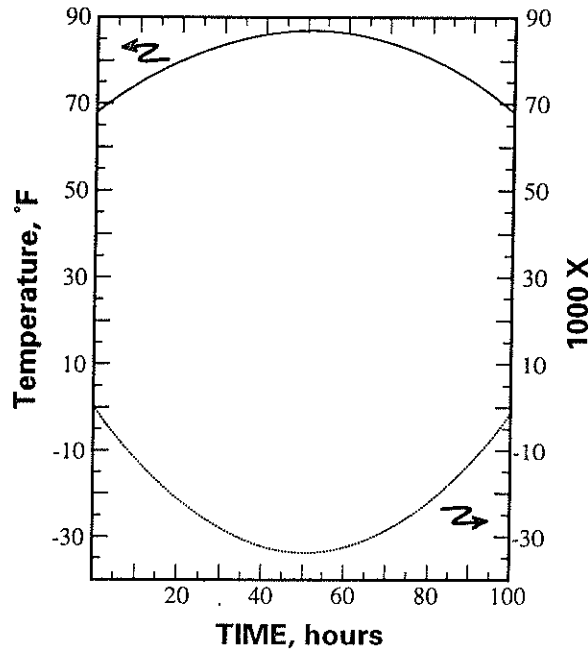


Figure 6 Temperature pulse shape as a function of time, t , in hours. Lower curve is $1000x$; upper curve is temperature in degrees Fahrenheit.

In an recent paper,¹⁴ the author considered a temperature pulse of the form

$$x = x_m \left[1 \pm \left\{ (t \pm m) / (t_s \pm m) \right\}^2 \right]$$

The pulse starts from $x = 0$ at time t_s , attains $x = x_m$ at time $t = m$ and returns to $x = 0$ at $t = t_e = 2m - t_s$. The pulse is symmetric about $t = m$. Figure 6 displays the dependence of both x and temperature on t . We assume $x_m < 0$, so the pulse in x is negative, corresponding to a positive pulse in T . Then a result was found that was equivalent to

$$\begin{aligned} F(t) \pm F(t_s) &= C \{ q(aV) + q(a) \pm 1 \} \\ u &= \pm E x_m, \quad a = (2u)^{1/2}, \quad V = (t \pm m) / (m \pm t_s) \\ C &= (m \pm t_s) (\pi/u)^{1/2} e^u, \end{aligned}$$

where q is the standard, normal cumulative function, provided $t_s < t < t_e$. In particular at the end of the pulse we have

$$F(t_e) - F(t_s) = C \{ 2q(a) - 1 \}$$

This formula shows that the F accumulated during the pulse is simply proportional to $m - t_s$ i.e., to the pulse width. Moreover, since E and x_m influence F only through the combination u , changes in E and x_m that lead to the same u also lead to the same

accumulated F . Although these results are specific to the temperature pulse assumed here, they are useful as a guide to what we might expect for pulses of generally similar shape. The author described formulas for an entire family of such pulses.¹⁴

An example

This fictitious example is about finding the shelf life, L , of a food item whose quality, A , varies with time according to the model of Equation (2) with $n = 0.2$, $c = 1 - n = 0.8$. The initial quality, at time $t_0 = 0$, is taken to be $A = A_0 = 100$ on some scale whose true meaning is irrelevant to the example. The item is expected to be stored at $68^\circ\text{F} = 20^\circ\text{C} = 293\text{ K}$ for 500 h or about 21 days. The item obeys Arrhenius kinetics with activation energy, E_a , of 20 kcal/mol. Then

$$T_r = 293$$

$$E = 20,000 / 293 / 1.986 = 34.37.$$

The quality is assumed to have $A_b = 40$, i.e., the item is unacceptable when A deteriorates to or below 40. Then

$$R_b = 0.4.$$

The rate constant, $k_r = k_0$, is found by solving Equation (6) in the form

$$\begin{aligned} k_r &= A_0^c (1 \pm R_b^c) / (cL) \\ &= 100^{0.8} (1 \pm 0.4^{0.8}) / [0.8(500)] = 0.05171. \end{aligned}$$

Thus at the reference temperature, 68°F ($T = T_r = 293$), we have

$$x = 0, k = k_r = 0.05171, L = 500\text{ h}.$$

The values of the rate constants and shelf lives for storage at other constant temperatures are found by applying the formula

$$k = k_r e^{\pm Ex}$$

to obtain k , and substituting in Equation (6)

$$L = A_0^c (1 \pm R_b^c) / (ck)$$

to find L . At $77^\circ\text{F} = 25^\circ\text{C} = 298\text{ K}$ we obtain

$$x = (293 / 298) \pm 1 = \pm 0.01678$$

$$k = (0.05171) e^{(34.37)(0.01678)} = 0.09205$$

$$L = 100^{0.8} (1 \pm 0.4^{0.8}) / [0.8(0.09205)] = 281\text{ h}.$$

Similarly at $86^\circ\text{F} = 30^\circ\text{C} = 303\text{ K}$ we obtain

$$x = \pm 0.03300, k = 0.16075, L = 161\text{ h.}$$

Now suppose that there has been a failure of the cooling system that controls the storage area, leading to a temperature pulse of the type considered at the end of the preceding section. We assume that the pulse commences at $t_s = 100\text{ h}$, reaches its maximum, 86°F or $x_m = -0.0330$, at $m = 150\text{ h}$, and returns to 68°F or $x = 0$ at $t = t_e = 200\text{ h}$. We want to determine the decreased shelf life resulting from this cooling failure. The formulas of the preceding section give

$$u = \pm Ex_m = \pm(34.37)(\pm 0.03300) = 1.1342$$

$$C = 50(\pi/1.1342)^{1/2} e^{1.1342} = 258.7$$

$$a = [2(1.1342)]^{1/2} = 1.506$$

$$q(a) = 0.934$$

$$F(t_e) \pm F(t_s) = 258.7[2(0.934) \pm 1] = 224.6\text{ h.}$$

Then the shelf life is found by solving

$$F_n = t_s + (L \pm t_e) + [F(t_e) \pm F(t_s)],$$

where F_n is the nominal or intended shelf life at $x = 0$, i.e., $F_n = 500$. This leads to

$$L = F_n + t_e \pm t_s \pm [F(t_e) \pm F(t_s)]$$

$$L = 500 + 200 \pm 100 \pm 224.6 = 375.4\text{ h.}$$

The effect of the pulse has therefore been to reduce L from its nominal value, 21 days, to about 16 days.

We might also ask about the effects that errors in estimating E_n have on the shelf life. This could be investigated by simply making several different calculations for various values of E . It might also be studied by carrying out a Taylor series expansion of Equation (8) in powers of $(E - E_n)$, where E_n is the nominal or intended value of E . Omitting the details, we find that

$$(\delta L) \approx \pm 5.6 (\delta E),$$

where (δL) is the change in L caused by the change (δE) in E . As expected, an increase in E causes a loss of shelf life.

Conclusions

The theory given above is reasonably complete as to the implications of the simplest and most used mathematical model. The "General Theory" Section of this chapter makes an

attempt to describe a framework into which a more complete theory might fit, but there seems not to have been much effort to go beyond the simple theory. Certainly, the situation where two or more interactions affect the quality is of importance, and assumptions other than Arrhenius kinetics may sometimes be appropriate.

As mentioned in the chapter's Introduction, this model must usually be combined with equations that determine the temperature in the food. This adds a formidable layer of difficulty to the entire problem. The temperature most often depends on both time and position within the food and is governed by one or more partial differential equations. These have to be solved to determine the time variation of the highest temperature in the food, which is then taken as $T(t)$. In many cases the solutions of the partial differential equations have to be carried out by numerical means and may be the most time-consuming part of the problem. The present review has completely ignored this aspect of quality loss estimation and focused entirely on the narrower and more manageable aspects that arise when $T(t)$ is known. However, if significant energy is absorbed or liberated during the chemical reactions that affect quality, it may be impossible to treat separately the quality loss and thermal parts of the problem.

It is clear that much remains to be done. Many of the recent attempts to deal with quality loss are computer-based, and this is to some degree inevitable. However, there are large bodies of mathematical theory dealing separately with quality loss and thermal variation, some portions of which may help to reduce the difficulty of these problems.

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